TRACE ELEMENTS IN ILLINOIS COALS BEFORE AND AFTER CONVENTIONAL COAL PREPARATION

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Keywords: trace elements, Illinois coals, cleaned coal

INTRODUCTION AND BACKGROUND

Responding to recent technological advances and renewed environmental concerns requires improved characterization of Illinois and other US coals. Much of the existing trace element data on Illinois coals are on channel samples; these data need to be supplemented with data on as-shipped coals. Such data will provide a factual basis for the assessment of noxious emissions at coal-fired electric power plants.

The Clean Air Act of 1990 [Public Law 101-549, 1990] identified many trace elements as "Hazardous Air Pollutants" (HAP) (Table 1). A parallel regulation is also underway in Illinois [Illinois Pollution Control Board, 1990]. All of these HAP elements are present in Illinois and other coals [Gluskoter et al., 1977; Harvey et al., 1983] in widely varying amounts. Utilities are presently exempt from having to consider emissions of trace elements; however, this may eventually change after the U.S. EPA completes its risk analyses and establishes emission standards. A database of trace element concentrations in the coals used by utilities is a prerequisite to defining the problem and establishing workable regulations.

Human sources constitute significant portions of the total global input of most trace elements into the atmosphere (Fig. 1). Emissions of trace elements from coal-fired power plants vary widely among countries and regions, reflecting varying trace element concentrations in coals from different sources. Among human sources, energy production (electrical utilities and industrial/domestic sector) is estimated to account for major portions of atmospheric emissions of Hg, Ni, Se, Sn, and V and lesser, but still significant, portions of As, Cd, Cr, Cu, Mn, and Sb. Oil combustion contributes larger portions of Ni, Sn, and V emissions than does coal combustion [Nriagu and Pacyna, 1988; Clarke and Sloss, 1992].

During combustion, trace elements in feed coals are partitioned among gas (flue gas), light particulate (fly ash), and slag/ash phases (Fig. 2). Typically, Hg, Br, Cl, F, and Rn end up in the flue gas; As, Cd, Ga, Ge, Pb, Sb, Sn, Te, Tl, and Zn in fly ash; and Eu, Hf, La, Mn, Rb, Sc, Sm, Th, and Zr in slag/ash deposits. Others show mixed affinities.

Swaine [1989] reviewed the environmental aspects of trace elements in coal. With respect to combustion, modern electrostatic precipitators can trap up to 99% of the fly ash. Swaine concluded that, in general, no trace element posed a significant environmental problem. This assumes that state-of-the-art electrostatic precipitators are used at the power plants and that the coals burned do not have exceptionally high concentrations of noxious elements that would be emitted in a gas phase. Deep physical cleaning of raw coal would reduce the levels of those elements that are associated with minerals [Capes et al., 1974; Gluskoter et al., 1977; Cavallaro et al., 1978; Norton and Markuszewski, 1989].

The purpose of this study was to determine trace element concentrations in as-shipped coals from Illinois mines, and compare the results with data on channel samples that represent coal in place prior to mining. Samples of 34 as-shipped samples were collected and analyzed for trace, minor and major elements, including the 18 HAP elements and others identified to be of greatest environmental concern by the U.S. National Committee for Geochemistry [1980]. Results on 20 of these elements of environmental concern are reported and discussed here. Radioactivity of the as-shipped coal samples was calculated from concentrations of U, Th, and K in the samples. Future work will concentrate on evaluating the further beneficiation of the as-shipped coal samples by fine coal cleaning.

EXPERIMENTAL

Samples and Sample Regions

Cleaned (as-shipped) samples of Illinois coals were collected from each of 33 preparation plants and from a mine that sells its coal after crushing. In most cases, the samples were splits from automatic samplers. Multiple cuts were taken across the coarse output belt over a period of 4 or more hours (commonly 8 to 24 hours) to obtain a representative sample. In some cases, the sample was collected from a stock pile, taking 15 to 20 widely spaced increments with a sampling shovel. All samples were sealed in 5 mil plastic bags or in 5 gallon plastic buckets and transported or mailed to our laboratory within two days. Within a week, the samples were homogenized riffled, crushed, and packaged at our sample preparation laboratory, according to the procedure described in Figure 3.

To maintain confidentiality of the results with respect to individual mines, the Illinois coal field was divided into five multi-county regions (Fig. 4); only the regions from which the samples came from were identified.

Analyses for Trace Elements

Each of the 34 samples was analyzed for trace, minor, and major elements. These elements, their method of analysis, and the precision and accuracy of the methods are shown in Table 2.

RESULTS AND DISCUSSION

Trace Element Database

Our computerized database contains trace element information on 900 samples (Table 3). Figure 5 identifies the 60 elements for which concentrations are available on many samples in the database. The most useful records are from the 222 channel or equivalent samples which represent coal in-place prior to mining and cleaning. Table 4 and Figure 6 give the averages and variabilities for 20 critical environmental elements for channel samples from Illinois.

Trace Elements and Radioactivity in 34 As-shipped Samples

The concentrations of most of the environmentally critical trace elements in the 34 as-shipped coals (Table 4) vary less widely than those in the channel samples (compare Figs. 6 and 7). Comparison of the data from channel samples and from cleaned coals indicates that conventional coal cleaning can reduce the state-wide mean concentrations of trace elements in channel samples up to 67% (Fig. 8), except for U (12% enrichment). The reduction in elemental concentrations results from the reduction of mineral matter and some leaching by the process water. The enrichment of U in the as-shipped samples relative to channel samples suggests that this element is primarily associated with the organic material. Harvey et. al [1983], who calculated organic affinities from washability tests for Illinois coals, also concluded that U had organic affinity. However, even if U were largely associated with the organic matter, it would likely be located in very fine mineral grains disseminated within the organic matter [Finkelman, 1981; Clarke and Sloss, 1992].

It should be pointed out that, for a given mine, channel samples do not necessarily represent those portions of the seam where feed coals for as-shipped samples were mined. Therefore, the average trends of trace element reductions observed in Figure 8 may not hold for individual mines, as Figure 9 indicates. Zinc enrichment shown in Figure 9 suggests that the channel samples had been preferentially taken from low-Zn parts of the seam in a mine from the NW coal region. Zinc is concentrated in structurally disturbed zones of the seam which are mined but were not channel-sampled.

Because the channel samples were analyzed for fluorine (F) by an old technique, which tends to underestimate F in many coal samples [Wong et al, 1992], the F data from the channel samples and from as-shipped coals cannot be compared to evaluate the fate of F during coal preparation. At present, F analysis is carried out according to Australian hydropyrolytic procedure standard AS1038.10.4-1989.

The natural radioactivity of coal, which is derived from the decay of Th-232, U-238 and U-235, and K-40, can be calculated from the observed masses (weights) of U, Th, and K [Cahill, ISGS, personal communication]. The calculated radioactivity data for coals agres with observed radioactive measurements [Coles et al., 1978]. Table 5 shows that for cleaned Illinois coals, the contribution to radioactivity from U and Th is relatively small compared to that from K, which contributes to background radioactivity not only in coal but in all natural environments.

SUMMARY AND CONCLUSIONS

A database on trace elements in channel samples of Illinois coals was used to show the degree of reduction of key environmental elements in 34 as-shipped coals from Illinois mines collected and analyzed for this study. The results indicate that the state-wide mean concentrations of all tested trace elements, except U, are reduced in the cleaned coals relative to those in the channel samples that represent coal in place prior to mining. Because elemental concentrations in coal vary widely from place to place and coal to coal, only mean concentrations from a large number of channel and as-shipped samples should be compared. Better yet, washability studies on individual samples should be done to assess the degree and limit of the removal of trace elements from coal during coal preparation.

ACKNOWLEDGEMENTS

We thank Illinois coal companies for their cooperation in obtaining samples of their as-shipped coals. We also thank H. H. Damberger and W. T. Frankie for their help in the collection of the samples. This research was funded in part by the Illinois Department of Energy and Natural Resources through its Coal Development Board and Illinois Clean Coal Institute and by the U.S. Department of Energy. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of IDENR, ICCI, and US DOE.

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Table 1. Elements analyzed in project samples

Elements regulated* and analyzed	Other elements analyzed
Antimony	Aluminum
Arsenic	Boron
Beryllium	Calcium
Cadmium	Carbon
Chlorine	Copper
Chromium	Hydrogen
Cobalt	Iron
Fluorine	Lithium
Lead	Molybdenum
Manganese	Nitrogen
Mercury	Oxygen
Nickel	Phosphorus
Polonium #	Potassium
Radium #	Silicon
Radon #	Sodium
Selenium	Sulfur
Thorium	Titanium
Uranium	Vanadium
	Zinc

* Regulated by Public Law 101-549, 1990
\# Radioactive isotopes of these elements were calculated from the analytical concentrations of Th and U.

Table 2. Relative precision and methods for minor and trace elements

Element	Relative Precision	%	Average detection limit	WDXRF	AAS	INAA	OEP	EDX	PyroIC
MINOR oxides									
Al_2O_3	ash	3	0.1 %	X					
CaO	ash	3	0.02 %	X					
Fe_2O_3	ash	3	0.01 %	X					
MgO	ash	5	0.1 %	X					
MnO	ash	5	0.01 %	X					
MnO	coal	7	3 ppm			X			
P_2O_5	ash	5	0.02 %	X					
K_2O	ash	2	0.01 %	X					
SiO_2	ash	1	0.1 %	X					
Na_2O	ash	5	0.05 %	X					
TiO_2	ash	3	0.01 %	X					
TRACE elements									
As	coal	7	1 ppm			X			
B	ash	15	10 ppm				X		
Be	ash	5	0.5 ppm				X		
Cd	ash	10	2.5 ppm		X				
Co	coal	5	0.3 ppm			X			
Cr	coal	10	7 ppm			X			
Cu	ash	5	2.5 ppm		X				
F	coal	10	20 ppm						X
Hg	coal	15	0.01 ppm		X**				
Li	ash	12	5 ppm		X				
Mo	ash	25	10 ppm					X	
Mo	ash	25	10 ppm				X		
Mo	coal	20	10 ppm			X			
Ni	ash	10	15 ppm		X				
Pb	ash	20	25 ppm		X				
Pb	ash	20	10 ppm				X		
Sb	coal	10	0.2 ppm			X			
Se	coal	10	2 ppm			X			
Th	coal	5	0.4 ppm			X			
U	coal	15	3 ppm			X			
V	ash	3	8 ppm				X		
Zn	ash	7	1.5 ppm		X				

* Method: WDXRF - wave length-dispersive x-ray fluorescence spectrometry
AAS - atomic absorption spectrometry
INAA - instrumental neutron activation analysis
OEP - optical emission (photographic) spectrometry
PyroIC- pyrohydrolysis and ion chromotography
** Hg by cold vapor atomic absorption spectrometry

Table 3. Summary of sample types and seams in the ISGS database on trace elements in coal

	Samples from Illinois	Other states	Total no. samples
SAMPLE TYPES			
Channel & equivalent	222	67	289
Bench (partial seam)	158	11	169
Float-sink fractions	77	20	97
Run-of-mine	20	17	37
As-shipped	47	8	55
Shales & coal associated rock	240	13	253
All types	764	136	900
SEAMS			
Herrin seam (Ill. no. 6)	473	4	477
Springfield seam (Ill. no. 5)	166	20	186
Colchester seam (Ill. no. 2)	50	5	55
Other seams & rocks	75	107	182

Table 4. Ash content (dry, wt%), heating value (dry, BTU/lb), and trace element concentrations (dry, milligram per million BTU (mg/MBTU)) in channel samples and in as-shipped coals from Illinois

Sample type	Region		ash	BTU/lb	As	B	Be	Cd	Co	Cr	Cu	F	Hg	Li	Mn	Mo	Ni	Pb	Sb	Se	Th	U	V	Zn
Channel	all	mean	12.4	12532	506	3778	63	132	227	651	481	2320	6	565	2419	389	702	1426	44	90	78	71	1037	9094
		stddev	3.4	646	814	1810	37	339	147	365	338	1458	5	610	2014	301	422	1561	45	49	40	54	707	21753
		cases	186	195	201	190	199	90	198	198	200	167	161	112	193	170	196	191	201	197	142	111	200	204
	all	mean	12.4	12535	497	3777	63	115	229	658	484	2420	6	518	2150	410	678	1464	43	90	78	73	1097	9292
	(excluding	stddev	3.4	660	732	1900	39	330	148	377	344	1541	4	560	1715	313	337	1591	44	48	39	56	728	23145
	NE)	cases	159	167	175	166	171	81	172	172	172	141	136	92	166	148	168	167	175	171	121	99	172	176
	NE	mean	12.8	12511	562	3781	66	286	211	605	464	1779	8	781	4075	252	848	1167	51	92	79	54	670	7849
		stddev	3.5	566	1254	1010	19	393	143	271	303	675	6	783	2824	134	745	1336	54	52	50	35	401	9148
	NW	mean	12.8	12278	605	5167	86	334	254	693	612	1978	7	480	2670	395	818	2178	62	94	75	75	1117	21346
		stddev	3.0	590	1021	1515	54	621	216	413	397	794	4	372	1606	274	435	2530	67	58	48	42	633	44374
	SC	mean	12.0	12706	450	3237	52	42	247	608	473	2079	6	744	2061	289	664	1115	35	76	76	47	945	4478
		stdev	4.4	722	514	1050	27	45	111	408	492	620	4	1019	1365	294	277	758	22	33	48	33	546	4759
	SE	mean	11.8	12838	605	2260	63	55	224	610	445	2870	6	439	1891	515	623	1761	43	92	75	85	1247	6529
		stdev	3.3	627	721	1181	35	55	129	331	217	2455	5	224	2039	384	294	1402	34	55	30	79	998	9586
	SW	mean	13.3	12210	214	5653	46	29	185	757	408	2699	5	434	2159	382	182	512	27	96	89	73	993	5465
		stdev	2.5	412	376	1494	13	22	95	360	132	892	3	297	1518	182	274	383	32	35	29	40	363	4882
As-shipped	all	mean	10.1	12952	263	3222	50	39	124	494	325	3325	3	334	1336	387	500	996	31	69	52	81	1088	3026
	(excluding	stddev	2.4	476	292	1649	21	48	49	240	96	1435	2	263	1198	125	197	915	25	34	16	66	569	3122
	NE)	cases	34	34	34	34	26	12	34	34	34	34	34	34	34	19	34	30	34	34	34	32	34	34
	NW	mean	9.7	12860	209	4918	64	53	94	404	338	3005	3	147	1964	390	491	1427	32	63	41	77	722	3935
		stddev	2.5	435	203	1378	33	67	33	136	106	726	2	89	2116	106	270	1633	26	30	11	77	224	4755
	SC	mean	9.8	13069	330	2283	41	32	159	437	334	3169	2	579	1031	173	527	969	41	52	59	33	944	3116
		stdev	3.3	523	220	372	11	0	77	133	128	1092	1	445	662	0	192	704	41	12	24	8	347	4097
	SE	mean	9.6	13193	354	1788	46	26	135	440	290	2981	5	366	936	422	458	1127	30	63	52	106	1281	2012
		stddev	2.0	402	408	635	8	13	34	72	64	834	2	143	354	103	142	817	15	22	10	81	692	1061
	SW	mean	11.9	12473	83	4639	46	24	105	805	368	4675	2	265	1545	377	567	406	16	109	60	100	1423	3587
		stddev	1.8	254	17	302	9	16	21	419	92	2664	0	73	487	154	200	109	6	50	12	26	600	1087

Table 5. Natural radioactivity in as-shipped Illinois coals

Region		Th (ppm)	Th-232 series * (Bq/kg)	U (ppm)	U-238 series ** (Bq/kg)	U-235 series*** (Bq/kg)	K (ppm)	K-40 (Bq/kg)
All	mean	1.5	6.0	2.2	27.8	0.68	2039	63.2
	stddev	0.4	1.6	1.9	24.0	0.59	792	24.6
NW	mean	1.2	4.7	2.1	25.6	0.6	1676	51.9
	stddev	0.3	1.2	2.3	28.0	0.7	427	13.2
SW	mean	1.6	6.6	2.7	33.7	0.82	2122	65.8
	stddev	0.3	1.1	0.7	8.5	0.21	1559	48.3
SC	mean	1.7	6.8	0.9	11.7	0.29	2225	69.0
	stddev	0.6	2.4	0.2	2.7	0.07	650	20.2
SE	mean	1.5	6.1	2.9	40.0	0.90	2163	67.0
	stddev	0.2	1.0	2.4	29.2	0.72	515	16.0

* Th232, Ra228, Ac228, Th228, Ta224, Rn220, Po216, Pb212, Bi212, Po212, Tl208
** U238, Th234, U234, Th230, Ta226, Rn222, Po218, Pb214, Bi214, Po214, Pb210, Bi210, Po210
*** U235, Th231, Pa231, Ac227, Th227, Ra223, Pb211, Bi211

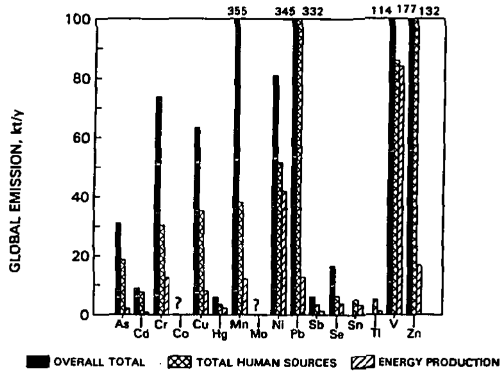

Figure 1. Global emissions of trace elements into atmosphere(after Nriagu, 1990).

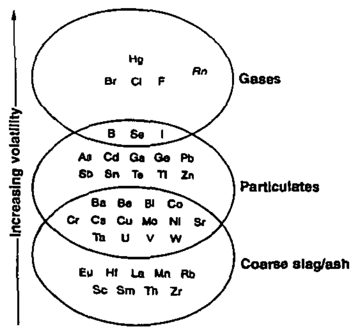

Figure 2. Behavior of trace elements during coal combustion and gasification (after Clarke and Sloss,1992).

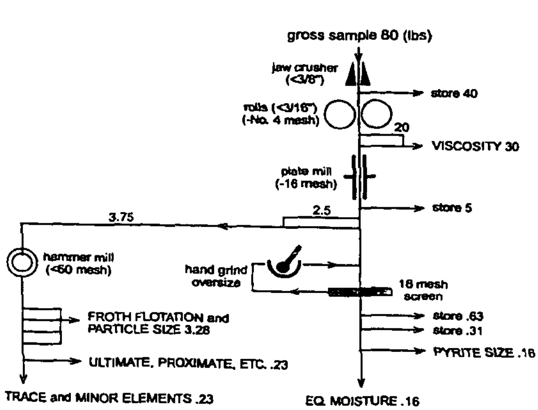

Figure 3. Flow chart for sample preparation. The weight (lbs) of the laboratory sample is given after the indicated test.

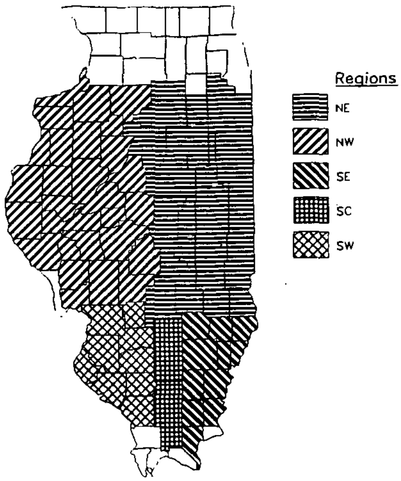

Figure 4. Sample regions of Illinois coal field.

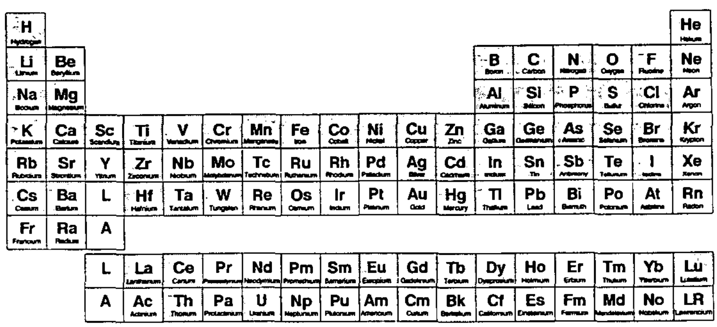

Figure 5. Analytical results on these 60 elements (shaded) are available for many sample-records in the ISGS database of trace elements in coal.

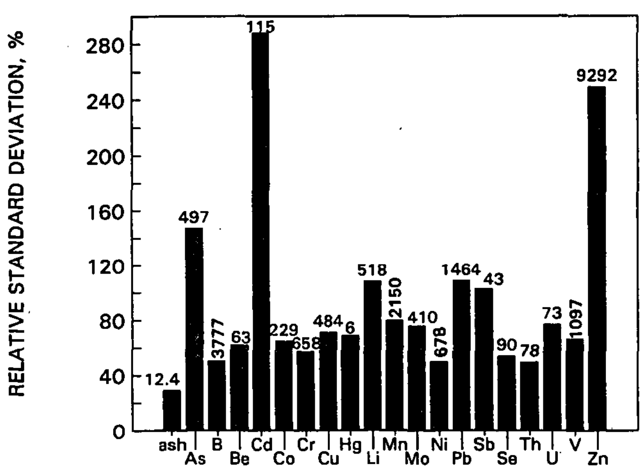

Figure 6. Variability of trace element concentrations in channel samples of Illinois coals, all regions (excluding NE region). Relative standard deviation was obtained by dividing standard deviation by mean and multiplying the result by 100. Numbers over bar indicate average concentrations of ash (wt%) or trace elements (mg/MBTU).

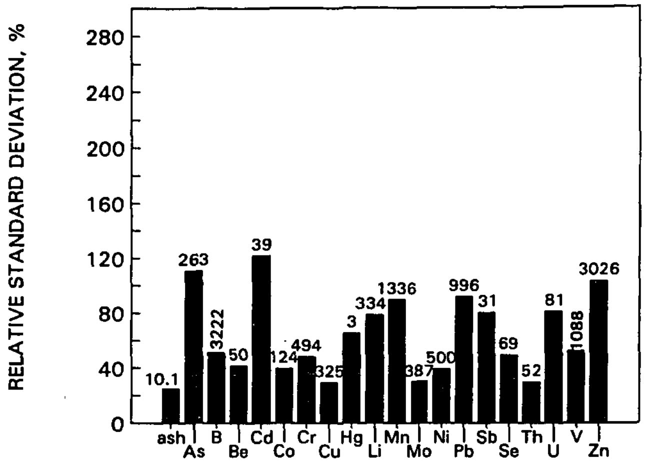

Figure 7. Variability of trace element concentrations in the 34 as-shipped coals, all regions (excluding NE region). Relative standard deviation was obtained by dividing standard deviation by mean and multiplying the result by 100. Numbers over bar indicate average concentrations of ash (wt%) or trace elements (mg/MBTU).

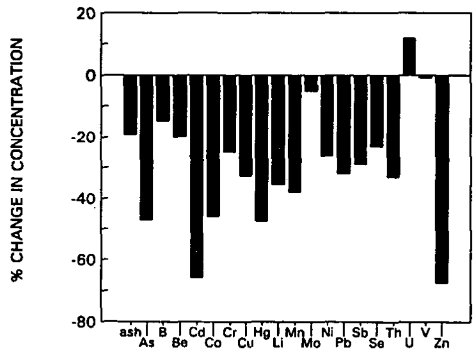

Figure 8. Reduction of trace element concentrations in as-shipped coals relative to those in the database channel samples, mean of state, excluding samples from NE region.

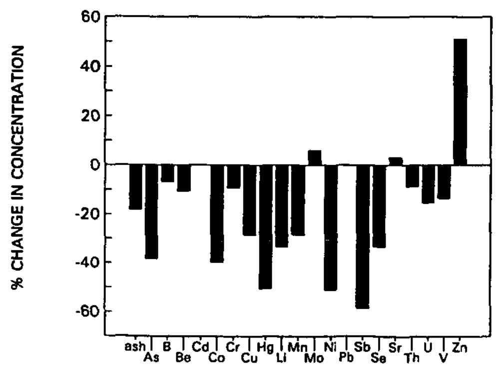

Figure 9. Reduction of trace element concentrations in the as-shipped coal relative to those in channel samples from a mine in the NW region. Data for Cd and Pb was not sufficient to compute the reduction for these two elements.